# Thermophysical Properties in the System Al<sub>2</sub>O<sub>3</sub>-MgO <sup>1</sup>

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### **ABSTACT**

Dense samples of two different Mg-Spinel and composites Alumina-Spinel and Magnesia-Spinel were prepared by powder metallurgy techniques and characterized using quantitative metallograpy, X-ray and electron microprobe analysis. On four kinds of pure Spinels the thermal conductivity was determined using thermal diffusivity measured together with heat-capacity and thermal expansion. The temperature functions of the Spinels show in the low temperature region the 1/a + bT-behaviour followed by nearly temperature independent thermal conductivities. Three stoichiometric Spinels show the same b-value (14.4  $\pm$ 0.2) m/W, while the non-stoichiometric compound of composition (Mg<sub>0.85</sub>, Al<sub>0.15</sub>) Al<sub>2</sub>O<sub>4</sub> shows a b-value of 10,6 m/W. The composites of the alumina rich compositions obey at low temperatures to the mixing rule. This is not the case for the Magnesia-rich side of phase composition. The high temperature thermal conductivity function of the composites shows a very complex behaviour.

**KEY WORDS:** thermophysical properties; thermal conductivity; thermal diffusivity; thermal expansion; specific heat capacity; composites; Spinel

#### 1. INTRODUCTION

The MgAl<sub>2</sub>O<sub>4</sub>-Spinel is a compound, which was of interest in fusion technology because of its dielectricity. The additional heating of the plasma with microwaves needs microwave windows of a material with low dielectric losses, suitable thermal conductivity and minor degradation of the physical and mechanical properties with irradiation.

Apart from this the quasi-binary system MgO-Al<sub>2</sub>O<sub>3</sub> shows interesting features with respect to heat transfer mechanisms. The pure Al<sub>2</sub>O<sub>3</sub> is a phonon conductor, the thermal resistivity is characterized by the three phonon Umklapp-Process, resulting in a linear temperature dependence for the thermal resistivity [1]. For MgO a combination of three and four phonon collisions was assigned to explain the temperature dependence of the thermal conductivity [2].

Furthermore the phase diagram of the MgO-Al<sub>2</sub>O<sub>3</sub> system shows a homogeneity range of the intermediate compound MgAl<sub>2</sub>O<sub>4</sub> in the high temperature region (Fig. 1), which may influence the thermal conductivity if deviations from stoichiometry of the Spinel are present.

The above shown characteristics of this quasi-binary system are the reasons for the detailed investigations presented in this paper.

## 2. SAMPLE PREPARATION

Samples were prepared as described in [4]. The starting powders were MgAl<sub>2</sub>O<sub>4</sub> (Baikowsky, France) with minor amounts of Al<sub>2</sub>O<sub>3</sub> (< 1 mass %) and MgO (1.3 mass %). Additions of Al<sub>2</sub>O<sub>3</sub> and MgO powders resulted in mixtures of the nominal compositions, 90, 80, 70, 60, 49, 40 and 20 mol % MgO and 10, 20, 30, 40, 51, 60 and

80 mol % Al<sub>2</sub>O<sub>3</sub> for densification by powder metallurgy techniques: isostatic compaction and sintering in air at 1650°C for 16.7 h.

Two commercial available kinds of stoichiometric MgAl<sub>2</sub>O<sub>4</sub> (Raytheon), single and polycrystalline samples were used to determine the thermophysical properties of the Spinelcompound in addition to those prepared by powder metallurgy techniques.

#### 3. SAMPLE CHARACTERIZATION

The characterization of the samples were performed to get information on the following topics:

- Nature, number and amount of phases in the specimen
- density and porosity
- stoichiometry and grain size of the pure Spinel.

All samples were prepared for quantitative metallography, i. e. grinding and polishing with diamond (15 - 1  $\mu$ m) and final polishing with SiO<sub>2</sub> (0,25  $\mu$ m). The measurements were performed on back scattered electron images, the phases were identified by the method of energy dispersive X-ray analysis (EDX). The pure Spinels were thermally etched at 1500°C for 2 h in air, their stoichiometry determined by electron microprobe and x-ray analysis.

The density was measured by the buoyancy method.

The results are summarized in Tab. 1 and 2. The theoretical densities in Tab. 1 are calculated from those of the pure components [5] with  $\rho A l_2 O_3 = 3.98 \text{ Mg/m}^3$ ,  $\rho M g O = 3.60 \text{ Mg/m}^3$ ,  $\rho M g A l_2 O_4 = 3.61 \text{ Mg/m}^3$ . While the data presented in Tab. 1 are clear and corresponds with the microstructure Fig. 2 and 3, the results presented in Tab. 2 will be discussed. Samples type F and G are single phase materials. Remarkable are the results

of the samples type F and G with respect to chemical composition, sample type F is nearly stoichiometric, while sample type G has a lower lattice constant a and the measured concentrations of the elements are: 45.26 w-% O; 14.80 w-% Mg and 39.94 w-% Al. The decrease of the lattice constant from F to G and the lower ionic radius of  $Al^{3+}$  compared to  $Mg^{2+}$ , lead to the supposition that a part of Al-atoms occupy the sites of Mg in the lattice; then a formula of the type  $(Mg_xAl_{1-x})A_2O_4$  results.

Regarding the grain size of the commercial Raytheon polycrystalline Spinel, this quantity cannot be described with one mean grain size, two maxima appear around 3  $\mu m$  and  $80 \ \mu m$ .

# 4. METHODS AND EQUIPMENT USED FOR THE DETERMINATION OF THERMOPHYSICAL PROPERTIES

The specific heat capacity of sample type RPC-Spinel was measured with a Netzsch DSC 404 up to 1300 K. Data were taken on heating with 20 K/min, sample weights were ~50 mg. It was checked whether the different stoichiometry of sample Type F and G of Spinel Compound causes possible difference in specific heat capacity using a Perkin Elmer DSC . No difference could be found.

The linear thermal expansion of the Spinel (RPC) was determined with a Netzsch Differential Dilatometer (402 ED) using the NIST Standard Reference material SRM 732. Data were taken on heating and cooling only at constant temperature and at constant absolute expansion. The heating rate between different temperatures was 2 K/min.

Thermal diffusivity measurements were performed with a laser flash equipment Theta Conductronic IV, using a Nd:glass laser and InSb, Ge an Si sensors. The analysis of the temperature increase of the rear side of the sample was done with the new Dusza Software LFE [6] to get the thermal diffusivity  $\alpha$ .

#### 5. EXPERIMENTAL RESULTS

The results for the specific heat capacity are shown in Fig. 4. The standard deviation for the Spinel data is  $\Delta c_p/c_p = 0.01$  up to 1300 K. The experimental curve of the relative linear thermal expansion of Spinel RPC together with those of MgO (recommend data in [9]) and Al<sub>2</sub>O<sub>3</sub> (NIST data of SRM 732) are presented in Fig. 5. The standard deviation for our data is given in the figure with markers at different temperatures.

The thermal diffusivity as a function of temperature is shown in Fig. 6. The standard deviation is  $\Delta\alpha/\alpha=4$  %. For conversion to thermal conductivity the following procedure was used:

$$\lambda = \alpha c_p \cdot \rho$$

( $\lambda$  -thermal conductivity,  $\alpha$  -thermal diffusivity,  $c_p$  -specific heat capacity,  $\rho$  -density) Each value of  $\alpha$  was multiplied with measured density (Tab. 1) and specific heat capacity at respective temperature. For the four Spinel compounds the data given in Fig. 4 were used. For composites sample type A to E the specific heat capacity was calculated with the mixing rule. Known temperature functions of  $c_p$  of the pure components and measured weight percentage of the present phases were used. All thermal conductivity data were corrected for zero porosity in using

$$\lambda_o = \lambda_p \left(1 - p\right)^{-3/2} \qquad [10] \qquad {}_{\scriptscriptstyle (1)}$$

( $\lambda$ o,  $\lambda$ p-thermal conductivity of dense and porous sample, p -porosity) Mean values of  $\lambda$  at each temperature T  $\pm$  1 K are shown in Fig. 7 for the Spinels, Fig. 8 for the Alumina rich composites and Fig. 9 for the Magnesia rich samples.

#### 6. DISCUSSION

The main topics of the discussion are: the temperature function of the conductivity and the behaviour of the composites with respect to thermal transport properties. In both cases the thermal resistivity is considered.

#### 6.1 THE THERMAL CONDUCTIVITY OF THE PURE SPINEL COMPOUNDS

Fig. 10 shows the thermal resistivity  $1/\lambda$  of the Spinel type F, G, RPC, RSC. For a common dielectric material it is expected that  $1/\lambda$  will follow the relationship  $1/\lambda = a+b$ T, where a represents the scattering due to point defects and b the scattering due to Umklapp-processes. For the four Spinel types the following b-values are calculated:  $14.6 \cdot 10^{-5}$  m/W (RSC),  $14.4 \cdot 10^{-5}$  m/W (RPC),  $14.2 \cdot 10^{-5}$  m/W (F). Therefore follows a mean value for stochiometric MgAl<sub>2</sub>O<sub>4</sub> of b=14.4 · 10<sup>-5</sup> m/W. The (Mg<sub>0.85</sub>Al<sub>0.15</sub>)Al<sub>2</sub>O<sub>4</sub> compound shows a value of  $10.6 \cdot 10^{-5}$  m/W, which is far away from the mean value for the stoichiometric compound. But all four sample types show a nearly temperature independent thermal conductivity from a certain temperature, indicating mixed heat transfer mechanisms.

We do not suppose a four phonon scattering process, because this would be expressed in a change of the transport mechanism at low temperatures [2]. It follows an internal radiation heat transfer, which is proportional to the optical constant, the crystallite size and the cube of temperature. Unfortunately the Raython polycrystal has a very complex

microstructure, as it can be seen in Fig. 11. It is not possible to describe the crystallite or grain size with one value. But the supposition that internal radiation has an important role in heat transfer of Mg-Spinel is consistent with the fact, that the single crystal will start its temperature independent behaviour of the thermal conductivity at the lowest temperature ( $\sim 800~\rm K$ ) of all sample types. One more reason for this assumption is the irradiation behaviour of the single crystal [11] shown in Fig. 12. Up to  $\sim 800~\rm K$  the thermal conductivity of the irradiated single crystal shows an expected decrease due to irradiation, but then the data join into the extrapolated low temperature behaviour represented by the 1/T relationship for  $\lambda$ .

#### **6.2 THE THERMAL CONDUCTIVITY OF THE COMPOSITES (TYPE A TO E)**

These are mixtures of either MgO and MgAl<sub>2</sub>O<sub>4</sub> (A to C) or of (Mg<sub>0.85</sub>Al<sub>0.15</sub>)Al<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> and should follow mixing rules, which change the thermal conductivity of the composites steadily and monotonically between the values of the pure phases. Because the values of the thermal conductivity of the pure phases are very close to each other (MgO at RT 48,4 w/mK,Al<sub>2</sub>O<sub>3</sub> 30.0 W/mK, MgAl<sub>2</sub>O<sub>4</sub> (F) 15.0 W/mK, (Mg<sub>0.85</sub>Al<sub>0.15</sub>) Al<sub>2</sub>O<sub>4</sub> (A) 11.6 W/mK), we checked our data of the composites only for the first order bounds, i. e. the parallel  $\lambda_{\parallel}$  and series array  $\lambda_{\perp}$  of the phases, Tab. 3. It shows the thermal conductivity of Alumina-Spinel composites within the first order bounds, but none of Magnesia-Spinel samples obey these bounds. In fact, it was not possible to prepare Magnesia as a dense and crack-free material under the same conditions as described above. Even a mixture corresponding to 90 mol-% MgO + 10 mol-Al<sub>2</sub>O<sub>3</sub> cracked totally. So it was decided to take the data given in [12] (as recommended values for high pure

single crystalline MgO). These data are obviously too high for the densified MgO being present in the composites treated in this paper. The temperature function of the thermal resistivity for the Alumina-Spinel composites (Fig. 14) follow the same type than that of the corresponding Spinel, a linear increase followed by a nearly constant behaviour. The thermal resistivity function of the Magnesia-Spinel composites (Fig. 15) cannot be explained here. The lack of knowledge in this part of the quasi-binary system Al<sub>2</sub>O<sub>3</sub>-MgO is too high at this time.

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Table 1:

Sample Type	A	В	С	D	E
nom. composition	80 MgO,	70 MgO,	60 MgO	20 MgO,	10 MgO,
mol %	$20 \text{ Al}_2\text{O}_3$	$30 \text{ Al}_2\text{O}_3$	40 Al <sub>2</sub> O <sub>3</sub>	80 Al <sub>2</sub> O <sub>3</sub>	90 Al <sub>2</sub> O <sub>3</sub>
phases	MgO +	MgO +	MgO +	Al <sub>2</sub> O <sub>3</sub> +	Al <sub>2</sub> O <sub>3</sub> +
	Spinel	Spinel	Spinel	Spinel	Spinel
vol. % Spinel	71	88	94	59	30
weight % Spinel	71	88	94	61	32
theor. density on	3.605	3.605	3.605	3.76	3.87
Mg/m <sup>3</sup>					
density in Mg/m <sup>3</sup>	3.42	3.39	3.51	3.74	3.87
porosity %	5	6	3	1	≈0

Table 2:

Sample Type	F	G	RPC	RSC
origin	this	this	Raytheon	Raytheon
	work	work	polycrystal	single cristal
lattice	0.807	0.8045	0.808	0.808
constant a in nm				
stoichiomety	MgAl <sub>1.99</sub> O <sub>3.99</sub>	$(Mg_{0.85}Al_{0.15})Al_2O_4$	Mg Al <sub>2</sub> O <sub>4</sub>	MgAl <sub>2</sub> O <sub>4</sub>
porosity %	1	1	≈ 0	≈ 0
grain size	6 μ	6 μ	3 μ, 60 μ	
density Mg/m <sup>2</sup>	3.56	3.57	3.60	3.60

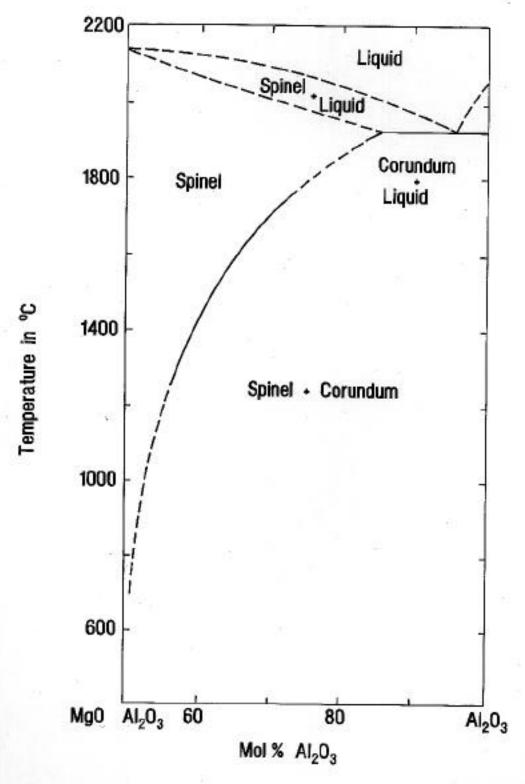
Table 3:

Composite	Vol % Spinel	λm	λ,,	$\lambda_{\perp}$
MgO	-	48.4	-	-
MgO-MgAl <sub>1.99</sub> O <sub>3.99</sub>	71	17.3	22.5	18.9
MgO-MgAl <sub>1.99</sub> O <sub>3.99</sub>	88	15.3	19.0	16.4
MgO-MgAl <sub>1.99</sub> O <sub>3.99</sub>	94	13.9	17.0	15.6
MgO-MgAl <sub>1.99</sub> O <sub>3.99</sub>	100	15.0	-	-
(Mg <sub>0.85</sub> Al <sub>0.15</sub> )Al <sub>2</sub> O <sub>4</sub>	100	11.6	-	
(Mg <sub>0.85</sub> Al <sub>0.15</sub> )Al <sub>2</sub> O <sub>4</sub> -	59	17.8	19.4	15.4
$Al_2O_3$				
(Mg <sub>0.85</sub> Al <sub>0.15</sub> )Al <sub>2</sub> O <sub>4</sub> -	30	24.0	24.5	20.3
$Al_2O_3$				
Al <sub>2</sub> O <sub>3</sub>	-	30.0	-	-

 $\lambda_m\text{-measured in W m}^{\text{-}1}~\text{K}^{\text{-}1}$ 

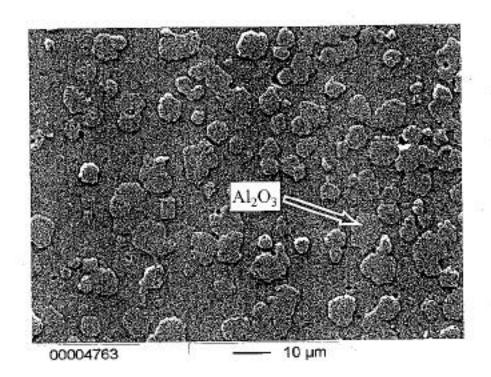
 $\lambda_{,,-}$ parallel arrray of phases

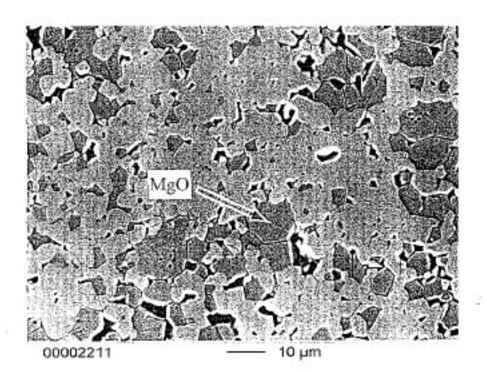
 $\lambda_{\!\scriptscriptstyle \perp}\text{-series}$  array of phases

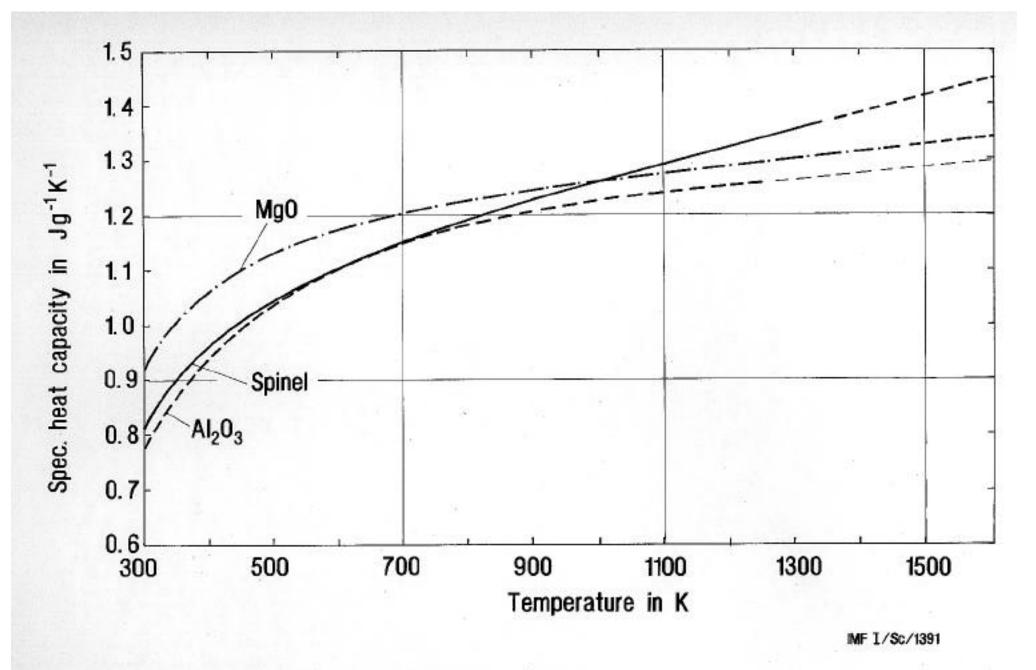


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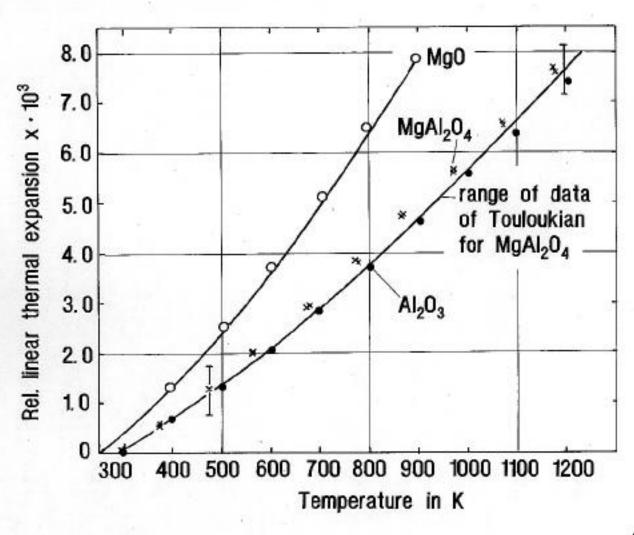
Alumina rich part of the phase diagram  $MgO - Al_2O_3$ 





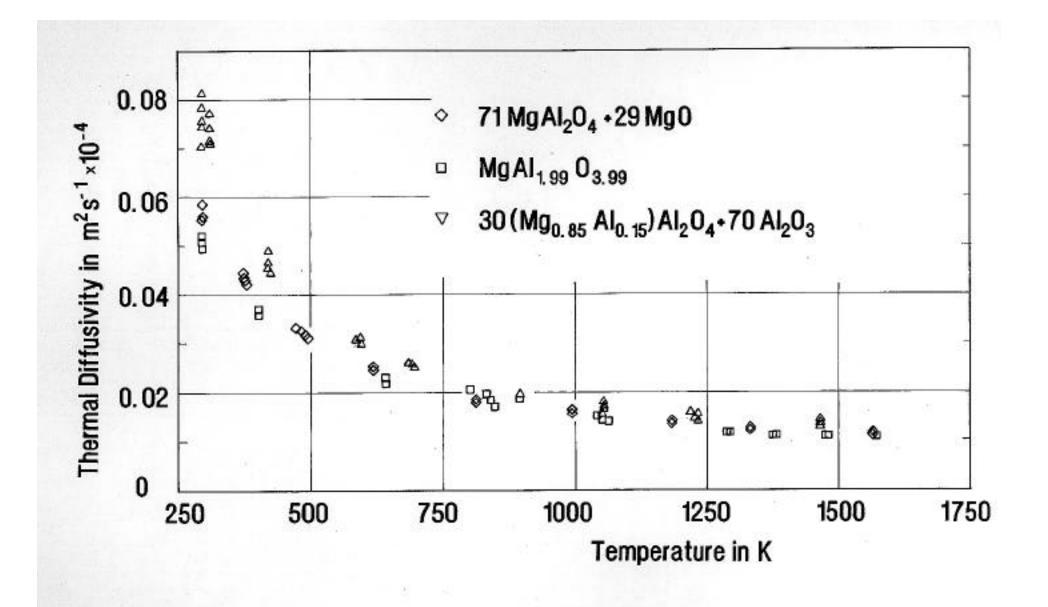


Specific heat capacity of MgO, Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub>

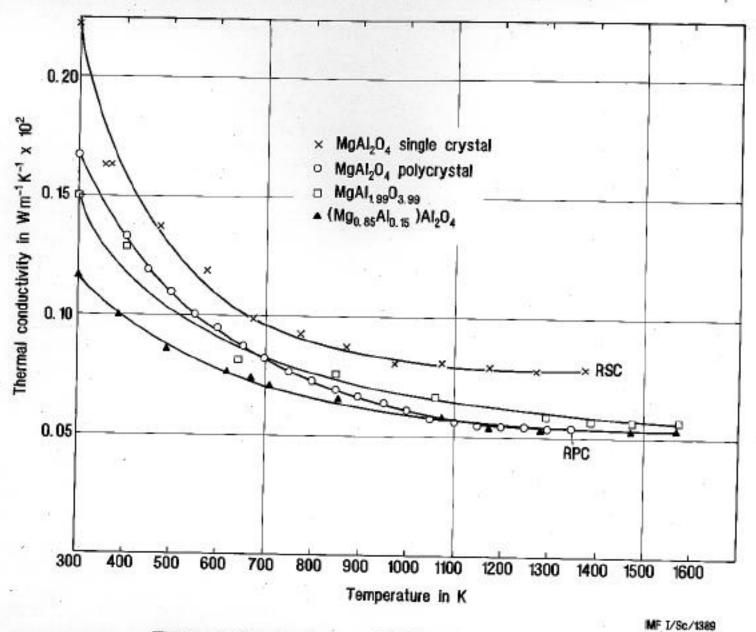


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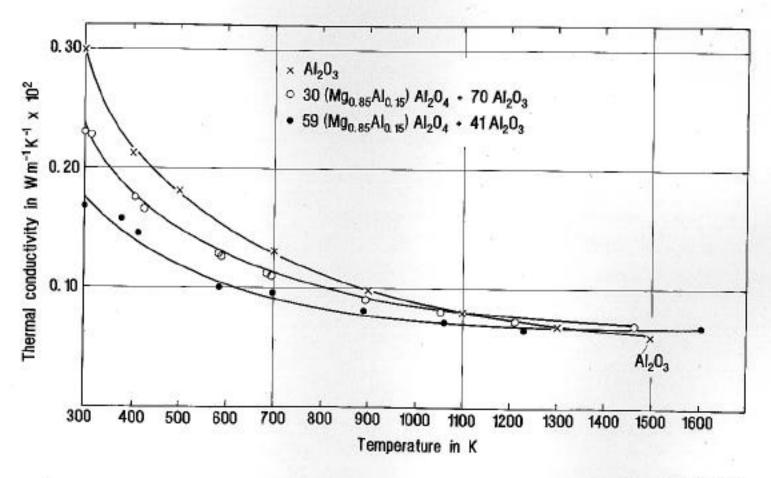
Thermal expansion of MgAl<sub>2</sub>O<sub>4</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>



Thermal Diffusivity of Samples in the System MgO-Al<sub>2</sub>O<sub>3</sub>

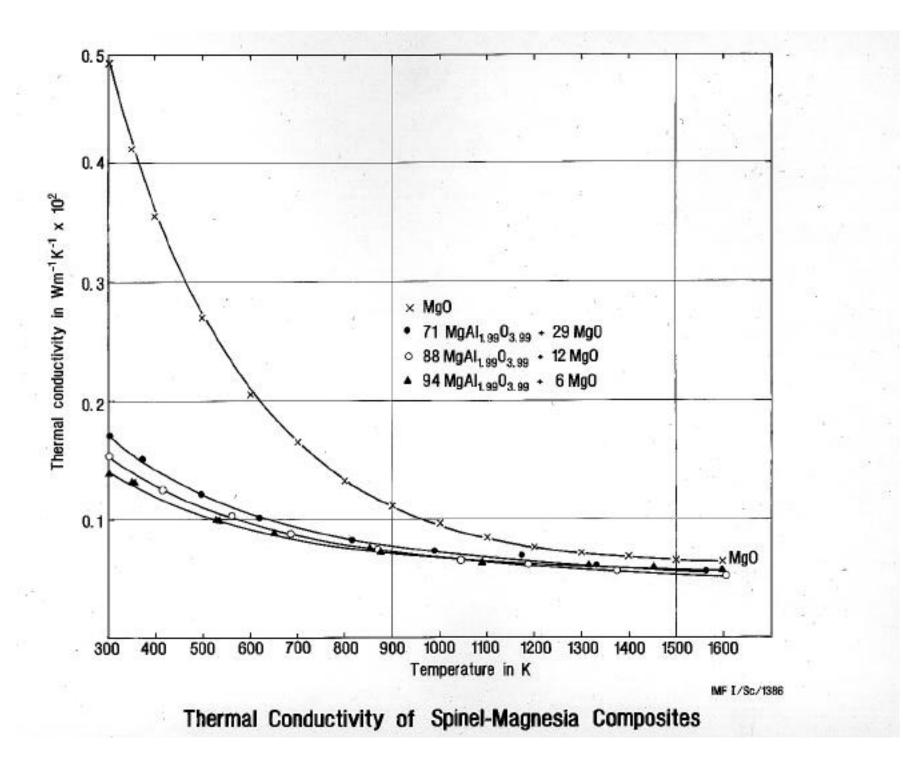


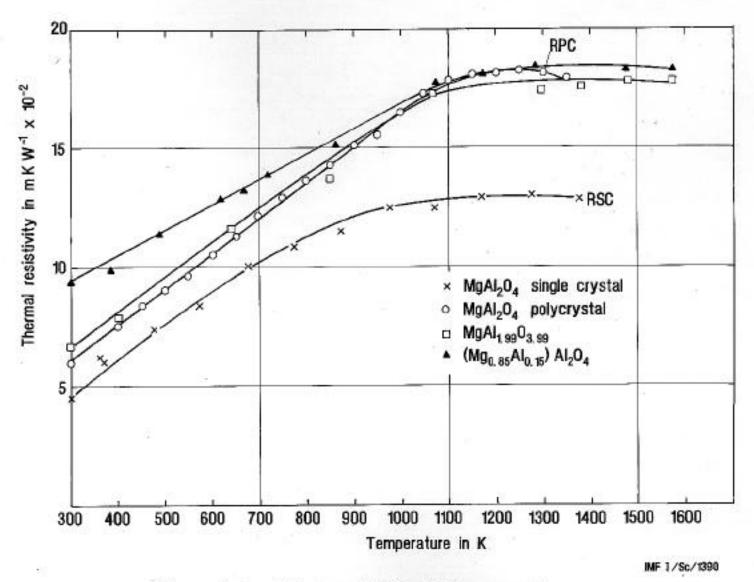
Thermal Conductivity of Spinel-Compounds



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Thermal Conductivity of Spinel-Alumina Composites





Thermal Resistivity of Spinel-Compounds

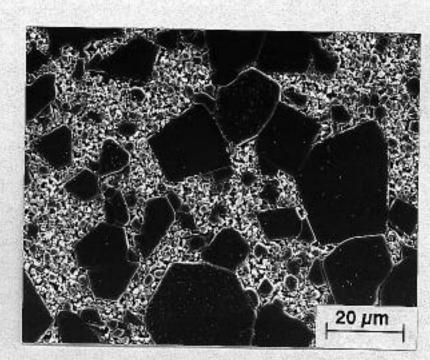
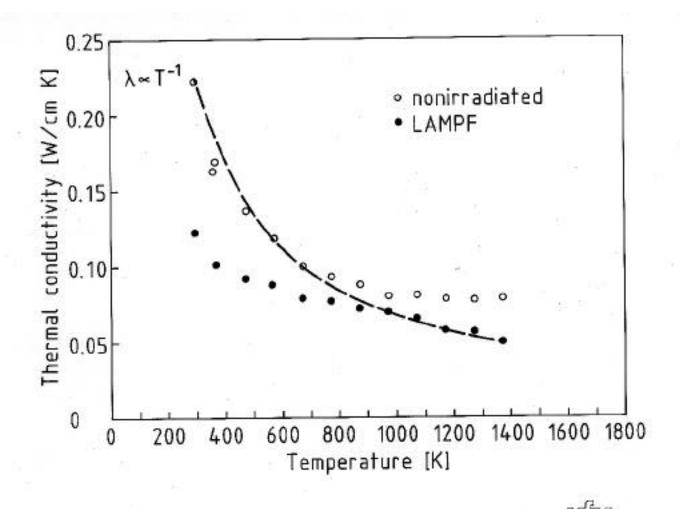
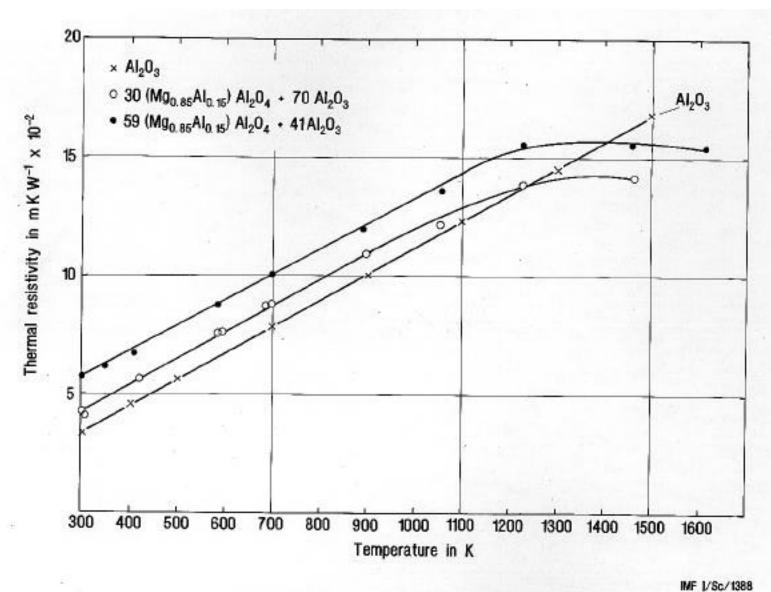


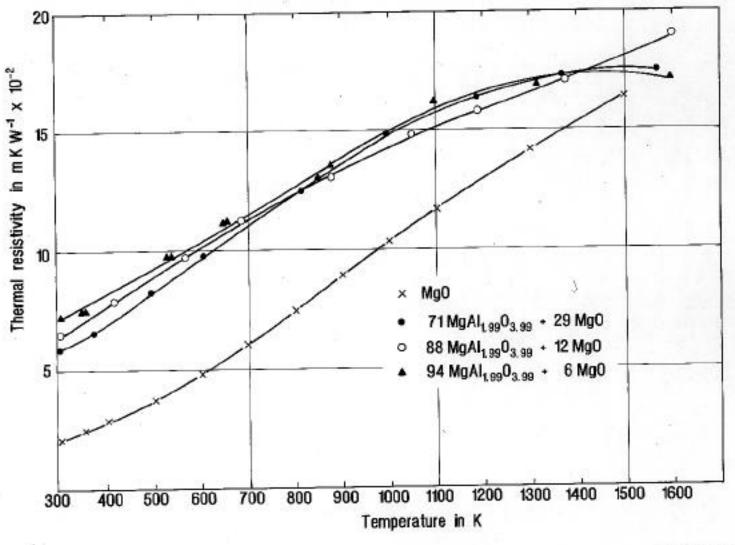
FIGURE 11



Thermal conductivity of nonirradiated and irradiated s.c.  ${\rm MgAl_2O_4}$ 



Thermal Resistivity of Spinel-Alumina Composites



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Thermal Resistivity of Spinel-Magnesia Composites